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(54) ELECTROLYTE-ELECTRODE UNIT FOR SOLID-ELECTROLYTE FUEL CELL AND PROCESS FOR THE MANUFACTURE THEREOF

(71) We, COMPAGNIE FRANCAISE
 DE RAFFINAGE, a French Body Corporate,
 5 rue Michel-Ange, 75016 Paris, France, do
 hereby declare the invention for which we
 pray that a patent may be granted to us and
 the method by which it is to be performed,
 to be particularly described in and by the
 following statement:—

The method and apparatus of the present
 invention concerns an electrolyte-electrode
 unit for fuel cell intended to operate at high
 temperature, and more particularly concerns
 a hermetic body of solid electrolyte which
 is a conductor of oxygen ions at high tempera-
 ture, and an electrode formed of at least one
 layer of doped indium oxide covering a part
 of the surface of the electrolyte and adhering
 to it.

Such units are already known in which the
 electrode is intended to operate as a cathode
 associated with a solid electrolyte of stabilized
 zirconia and a suitable metal anode, for
 instance a nickel anode, in a fuel cell having
 an operating temperature of about 800 to
 1100°C.

The effective use of doped indium oxide to
 form the cathode in such a fuel cell, if it
 can be achieved, constitutes an important
 advance over the prior art. Doped indium
 oxide is a relatively inexpensive material
 which is insensitive to the combustion support-
 ing gas. Even at the high operating tempera-
 tures of the cell, it has good chemical com-
 patibility with stabilized zirconia and has a
 coefficient of thermal expansion close to that
 of the latter. Moreover, its electrochemical
 properties are comparable to those of the
 metals which are best suited, namely the
 precious metals. The result is that the use
 of a doped indium oxide cathode instead of a
 cathode of precious metal, for instance
 platinum or silver, in a fuel cell of the type
 indicated above makes it possible considerably
 to improve the life and dependability in

operation thereof while lowering the cost 45
 of its manufacture.

However, the practical embodiment of a
 fuel cell comprising a doped indium oxide
 cathode and having electrical properties com-
 parable to those of cells comprising a cathode
 of precious metal, and also having a rather
 high power/weight ratio, encounters the
 following obstacle which up to now appeared
 to be unsurmountable.

In order to make it possible to obtain a
 sufficient power/weight ratio, it is necessary
 that the thickness of the layer of doped indium
 oxide not exceed a value of 150 to 200
 microns. This limitation seems to result
 in the necessity of making the indium oxide
 layer in compact form so that its actual resis-
 tivity does not excessively exceed the theoret-
 ical resistivity of the material itself. As a matter
 of fact, the value of the latter is only slightly
 less than the maximum value of resistivity for
 which the lateral resistance (resistivity/thick-
 ness ratio) of a layer, having a thickness not
 exceeding the upper limits indicated above,
 would be sufficiently small to permit the drain-
 age of the electrical current produced by the
 cell without the aid of a metallic current-
 collecting layer.

Now, a compact structure of the doped
 indium oxide layer is incompatible with good
 electrochemical operation of the cell. As a
 matter of fact, it is indispensable for said
 layer to have good permeability to the com-
 bustion supporting gas in order to permit the
 latter readily to arrive in contact with the
 electrolyte. A compact structure furthermore
 would not be satisfactory from the point of
 view of the number of electrochemically active
 triple points, that is to say, parts of the elec-
 trode in which the gas, in the present case
 the combustion supporting gas, is simultane-
 ously in contact with the electrode and the
 electrolyte. In order for the number of triple
 points to be sufficient, in other words, for
 the active surface/total surface ratio of the

[Price 25p]

electrode to, be sufficiently high, it is important that the electrode have, at least in the part thereof which is in contact with the electrolyte, as fine a granular structure as possible.

It therefore seemed that a layer of doped indium oxide having good permeability to gases and a fine porous structure which are indispensable for proper electrochemical operation of the cell would have too high a resistivity to permit its use with a thickness low enough for the weight/power ratio of the cell to be tolerable.

The present invention specifically makes it possible to reconcile the above requirements by simultaneously conferring all the necessary qualities on the cathode.

For this purpose, an electrolyte-electrode unit is constructed in accordance with the present invention by forming the layer of doped indium oxide with dendrites whose principal axes are substantially perpendicular to the surface of the electrolyte; these axes forming trunks having a diameter of between 500 and 1500 Å, so that said layer is permeable to gas; and by having the thickness of this layer at most equal to 0.02 cm.

It is due to the very special structure which has just been defined that the electrode forming part of the electrolyte-electrode unit has a sufficient permeability to gases and a particularly high ratio of active surface to total surface while having a sufficiently low resistivity, of less than 7.5×10^{-3} ohm.cm, that its lateral resistance does not exceed 0.5 ohm (practical limit) for a thickness at most equal to 0.015 cm.

In a variant of the electrolyte-electrode unit, according to an alternative embodiment of the present invention, the electrode comprises, between the electrolyte and the doped indium oxide layer, a porous layer formed of granules of at least one chromite of at least one element selected from among the rare earths and yttrium, of the general formula:



in which T represents at least one rare earth or yttrium or a mixture of these elements, x, a and b being numbers between 0 and 1 which can assume a value of 0 and the values of which satisfy the equation

$$a+b=x,$$

there granules being fastened to the electrolyte over at least a part of the surface thereof in contact with it, the indium oxide layer being arranged in such a manner as to form an electric contact between all of these granules.

The presence of the chromite layer eliminates the risk of diffusion of the indium oxide into the electrolyte and moreover increases the

adherence of the layer of indium oxide on the surface of the electrolyte. Thus, this layer further improves the life and the reliability in operation of the cell. Furthermore, this layer increases the catalytic activity of the cathode, which improves the performance of the cell, all other things being equal.

As the doping element for the indium oxide one may include at least one of the elements whose use is already known; particularly antimony, tellurium, gallium, zinc, tin, cadmium, germanium, tantalum, titanium, tungsten, chlorine and fluorine.

The doping element is preferably tin and more particularly in a proportion of between 1 and 5 atom %, referred to the total number of indium and tin atoms.

As solid electrolyte, which is a conductor of oxygen ions at high temperature, there may be used any known suitable material, for example, zirconia stabilized in the form of a cubic solid solution comprising, in addition to ZrO_2 and a certain proportion of hafnium oxide coming from the presence of the latter element in zirconium ores, at least one stabilizing oxide selected, for instance, from among the oxides of the elements Ca, Y, Sc, rare earths and mixtures of said oxides, in particular mixtures of rare earth oxides.

With respect to the shape of the hermetic body of solid electrolyte, it may be any of the known shapes, such as that of a disk or tube. The dimensions of this body, and in particular its thickness, may also be selected freely in accordance with the general configuration of the cell, respecting the known criteria applicable to the construction of this type of cell.

Preferably the porous chromite layer is formed of a chromite or a mixture of rare earth chromite having a coefficient of expansion which is as close as possible to that of the electrolyte. Thus, for instance, in the event that the electrolyte is stabilized zirconia, one preferably employs lanthanum chromite and more particularly lanthanum chromite doped with strontium, particularly the one having the formula:



The average dimensions of the chromite granules are preferably of the order of 0.05 to 2 microns and the thickness of the intermediate layer formed by these granules is between about 0.5 and 2 microns.

Another embodiment of the invention is a method of manufacturing the electrolyte-electrode unit which has just been described. This method is characterized by placing in a hermetic enclosure a target (having the composition which it is desired to confer upon the layer of doped indium oxide) and the electrolyte, reducing the pressure prevailing

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in the enclosure down to a pressure of between 10^{-3} and 10^{-2} mm Hg, heating the electrolyte at least equal to 300°C , and vaporizing the material of the target by electronic bombardment in such a manner as to obtain a deposit of a doped indium oxide layer on the surface of the electrolyte.

The power of the beam of electrons used to effect the electronic bombardment is preferably adjusted to a value sufficient to obtain a rate of growth in thickness of the indium oxide layer of between 1 and 10 microns per minute.

During the depositing, the electrolyte can be given a suitable displacement, for instance a rotation around an axis and/or an oscillation parallel to a given direction, which may be identical with the axis of rotation, in order to obtain good homogeneity and uniform thickness of the layer of doped indium oxide which is deposited on the electrolyte.

One can also in known manner impart any suitable displacement to the target with respect to the impact of the beam of electrons, for instance a spiral displacement of said impact on the target, particularly for having a uniform target temperature during the deposition.

In accordance with one particular embodiment of the method described above, the purpose of which is to manufacture an electrolyte-electrode unit according to the variant in which the electrode comprises, in addition to the indium oxide layer, also a porous layer of chromite, one operates in the following manner:

Into a hermetic enclosure there is placed a target formed of at least one chromite of at least one element selected from the rare earths and yttrium, of the general formula:



in which T represents at least one rare earth or yttrium, or a mixture of these elements, x , a and b being numbers between 0 and 1, which can assume a value of 0 and which satisfy the equation

$$a+b=x,$$

and the electrolyte. The pressure prevailing in the enclosure is decreased to a pressure close to 10^{-4} mm Hg. The electrolyte is heated to a temperature at least equal to 300°C . The material of the target is vaporized by electronic bombardment so as to deposit a layer formed of chromite granules on the surface of the electrolyte. Whereupon a layer of doped indium oxide of dendritic structure is deposited on the free surface of said layer, proceeding in the manner described above. Finally, at least the layer of chromite is fired at a temperature of between 600 and 1400°C after the depositing of the intermediate layer or

after the depositing of the layer of indium oxide.

Example 1

A sintered body of indium oxide doped with tin, of a composition corresponding to a mixture containing 98 mol % In_2O_3 and 2 mol % SnO_2 , in the form of a cylinder of 20 mm diameter and 40 mm height, intended to serve as target, is prepared in the following manner: the two above oxides are mixed together in the form of fine powders while crushing them together so as further to reduce their particle size to an average value of the order of 20 to 50 microns. A cylinder corresponding to the final dimensions desired is then formed by isostatic pressing, and this cylinder is sintered at 1000°C in an air atmosphere for 12 hours.

As electrolyte there is used a tube of zirconia stabilized with ytterbium, having the molar composition of ZrO_2 (HfO_2) 90 mol %; Yb_2O_3 10 mol %, and a length of 20 mm, outside diameter of 8 mm, and thickness of 0.2 mm.

The target and the electrolyte tube are placed in a vacuum evaporation-condensation apparatus comprising essentially a hermetic bell within which the pressure can, by means of a suitable pumping device, be brought to and maintained at a pressure not exceeding 2×10^{-6} mm Hg, and an electron gun capable of delivering a beam having a maximum power of 2 kw with a diameter of 16 mm at the point of impact on a target.

The doped indium oxide cylinder constituting the target is placed with its axis vertically on a support formed of a small copper crucible cooled by internal circulation of cold water. The electrolyte tube is placed on a moving heating support which imparts to it a movement of rotation at a speed of 1 rpm around its axis at an average distance of 10 cm from the target, the axis of the tube being horizontal. A removable mask is interposed, at the start of the operations, between the target and the electrolyte tube.

The air is first of all removed from the vacuum enclosure down to a pressure of 2×10^{-6} mm Hg, whereupon a stream of pure oxygen is introduced so as to increase the pressure to 10^{-4} mm Hg. The bombardment of the target is then started with a beam power equal to 1 kw, the impact on the target having an area of 200 mm^2 . In this way the temperature of the target in the region around the impact is brought to about 1000°C , which temperature is maintained for 10 minutes. The power of the electron beam is then brought to 2 kw so as to increase the temperature of the target within the zone of impact to about 2000°C . The pressure is allowed to rise by itself to 10^{-3} mm Hg in the enclosure and the mask is retracted so as to place the electrolyte tube in sight of the target. The surface

temperature of the electrolyte is maintained at about 600°C. In this way a homogeneous, microporous, dendritic layer of a very uniform thickness is deposited on the entire outer surface of the electrolyte tube with a rate of deposition of between 5 and 10 microns per minute. At the end of 20 minutes there is thus obtained a layer of a total thickness of 150 microns. The very uniform dendritic structure of this layer is shown by examination with an electron microscope with stereoscopic sweep.

Example 2

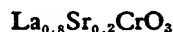
The same procedure was used as in Example 1, but instead of depositing the layer of indium oxide doped with tin directly on the surface of the solid electrolyte tube, there was first deposited on said surface a layer of lanthanum chromite doped with strontium, having a composition corresponding to the formula



with constant thickness of about 2 microns covering the entire outer surface of the electrolyte tube.

For this purpose, a target of lanthanum chromite doped with strontium having the composition indicated above was first of all prepared by sintering in the form of a cube having a side of 1 cm. For the preparation of this target, the following procedure was employed:

Lanthanum oxide La_2O_3 and strontium nitrate $\text{Sr}(\text{NO}_3)_2$ were homogeneously mixed in the form of powders in proportions corresponding to an atomic ratio of lanthanum to strontium of 4, and this mixture was calcined in air at 600°C until no further nitrous vapors were given off. To the resultant powder there was added an amount of chromium oxide Cr_2O_3 in powder form corresponding to the atomic composition represented by the formula



and the mixture of powder thus obtained was crushed so as to make it perfectly homogeneous while decreasing its particle size to an average value of the order of 30 microns.

A cylinder of dimensions corresponding to the final dimensions indicated above was then formed by isostatic pressing under a pressure of 50 tons/cm² and this cylinder was sintered at 1600°C in air for 2 hours. The cylinder was then again crushed in order to obtain a powder having a particle size of an average of about 100 microns, whereupon this powder was compressed under a pressure of 12 tons/cm² so as to form a cube of a side of 1 cm and this cube was sintered for 4 hours at 1900°C in air.

The doped lanthanum chromite target was placed on the target support in the vacuum enclosure and a layer of doped lanthanum chromite having a thickness of about 2 microns was deposited on the outer surface of the tube of solid electrolyte by evaporation-condensation under the following operating conditions:

pressure within the enclosure	10 ⁻⁴ mm Hg	
power of the beam of electrons	10 watts/mm ²	70
distance between the target and the solid electrolyte tube	18 cm	
surface temperature of the electrolyte tube	450°C	

The other operating conditions are the same as in the case of the deposit of the doped indium oxide layer described in Example 1.

The electrolyte tube, covered with the layer of lanthanum chromite, was then heated in air for 2 hours at 950°C.

The layer of doped lanthanum chromite thus deposited on the electrolyte is formed of approximately spherical granules strongly adhering to the electrolyte and to each other, with an average diameter of about 0.5 micron, leaving between them communicating pores having approximately the same dimensions as the grains.

A layer of indium oxide of dendritic structure was deposited in the surface of said porous lanthanum chromite layer by the same procedure as indicated in Example 1.

Example 3

The same procedure was used as in Example 2, effecting in succession a deposit of a layer of lanthanum chromite and then of a layer of doped indium oxide, but instead of heating the tube in air after the depositing of the first layer, this operation was carried out under the same conditions as in Example 2 after the depositing of the doped indium oxide layer.

WHAT WE CLAIM IS:—

1. An electrolyte-electrode device for a high temperature fuel cell comprising a body of solid electrolyte which is a conductor of oxygen ions at high temperature, and adhering thereto an electrode formed of at least one layer of doped indium oxide covering a part of the surface of the electrolyte, said layer of doped indium oxide having dendrites formed therein, the principal axes of which dendrites are substantially perpendicular to the surface of the electrolyte, these axes forming trunks having a diameter of between 500 and 1500 Å, so that said layer is permeable to gas, and the thickness of said layer is at most equal to 0.02 cm.

2. A device according to Claim 1, further comprising as a part of said electrode and formed between the electrolyte and said layer

of doped indium oxide, a porous layer formed of granules of at least one chromite of at least one element selected from among the rare earths and yttrium, of the general formula:



in which T represents at least one rare earth or yttrium, or a mixture of said elements, x , a and b being numbers between 0 and 1, and which may assume a value of 0 and satisfy the equation

$$a+b=x,$$

these granules being firmly attached to the electrolyte over at least a part of their surface in contact with it, the doped indium oxide layer being disposed in such a manner as to form an electric contact between all of these granules.

3. A device according to claim 2, wherein the said chromite granules have a particle size of between 0.1 and 0.5 microns and the thickness of the layer formed by said granules is between 0.5 and 2 microns.

4. A device according to either of claims 2 and 3 wherein the said chromite is



5. A device according to any one of the preceding claims, wherein the said indium oxide is doped by at least one of the following elements: antimony, tellurium, gallium, zinc, tin, cadmium, germanium, tantalum, titanium, tungsten, chlorine and fluorine.

6. A device according to claim 5, wherein the said indium oxide is doped by tin, the proportion of said latter element being at least 1% and at most 5% by atoms, referred to the total number of indium and tin atoms.

7. A device according to any one of the preceding claims, wherein said electrolyte is formed of stabilized zirconia.

8. A fuel cell including an electrolyte-electrode device according to any one of claims 1 to 7, the said doped indium oxide being a cathode, and the fuel cell being designed for an operative range of 800° to 1100°C.

9. A method for producing combined solid electrolyte-electrode structures for fuel cells wherein the electrode is a thin layer of 0.02 cm or less of doped indium oxide adherent to the electrolyte and having dendrites whose principal axes are substantially perpendicular to the surface of the electrolyte with the axes forming trunks having a diameter of between 500 and 1500 Å, comprising the steps of a method of placing in a hermetic enclosure the electrolyte and a target having the composition which it is desired to impart to the doped indium oxide layer, lowering the pressure prevailing in the enclosure to a pressure of between 10^{-3} and 10^{-2} mm Hg, heating the

electrolyte to a temperature at least equal to 300°C, and vaporizing the material of the target by electronic bombardment so as to obtain a deposit of a layer of doped indium oxide on the surface of the electrolyte.

10. A method according to claim 9 for producing said solid electrolyte-electrode structure with a chromite layer between said indium oxide layer and said electrolyte which is a porous layer formed of granules of at least one chromite of at least one element selected from among the rare earths and yttrium, said chromite having the general formula:



in which T represents at least one rare earth or yttrium, or a mixture of said elements, x , a and b being numbers between 0 and 1 which can assume a value of 0 and satisfy the equation

$$a+b=x,$$

these granules being firmly attached to the electrolyte on at least a part of their surface in contact with it and the layer of doped indium oxide being disposed in such a manner as to form an electric contact between all of said granules, comprising the additional steps prior to depositing the layer of doped indium oxide with dendritic structure of placing the electrolyte and a target formed of the said chromite in a hermetic enclosure, and decreasing the pressure prevailing in the enclosure to close to 10^{-4} mm Hg, heating the electrolyte to a temperature at least equal to 300°C, and vaporizing the material of the target by electronic bombardment so as to deposit on the surface of the electrolyte a layer formed of chromite granules, thereafter depositing the layer of doped indium oxide on the surface of the layer of chromite granules.

11. A method according to claim 10, wherein the chromite granules have a particle size of between 0.1 and 0.5 microns and are deposited so that the thickness of the layer formed by said granules is between 0.5 and 2 microns.

12. A method according to either of claims 10 and 11 comprising the further step of firing at least the layer of chromite at a temperature between 600 and 1400°C.

13. A method according to any one of claims 10 to 12 wherein the said chromite is



14. A method according to any one of claims 9 to 13, wherein the power of the beam of electrons causing said electronic bombardment is adjusted to give a rate of growth in thickness of the indium oxide layer of about 1 to 10 microns per minute.

15. A method according to any one of claims 9 to 14 wherein the indium oxide has been doped by at least one of the following elements: antimony, tellurium, gallium, zinc, 5 tin, cadmium, germanium, tantalum, titanium, tungsten, chlorine and fluorine.
16. A method according to claim 15, wherein the indium oxide has been doped by 10 tin, the proportion of the later element being at least 1% and at most 5% by atoms, referred to the total number of indium and tin atoms.
17. A method according to any one of 15 claims 9 to 16, wherein the electrolyte is formed of stabilized zirconia.
18. A method according to claim 9 substantially as hereinbefore described in any one of the Examples.
19. An electrolyte-electrode structure that has been produced by a method according to any one of claims 9 to 18. 20
20. A fuel cell being designed for an operative range of 800 to 1100°C including an electrolyte-electrode structure as claimed in claim 19. 25
21. An electrolyte-electrode device as claimed in claim 1 substantially as hereinbefore described in any one of the Examples.

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